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Dynamic operation and modelling of amine-based CO_2 capture at pilot scale

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ABSTRACT

This study combines pilot plant experiments and dynamic modelling to gain insight into the interaction between key process parameters in producing the dynamic response of an amine-based CO_2 capture process. Three dynamic scenarios from the UKCCSRC PACT pilot plant are presented: (i) partial load stripping, (ii) capture plant ramping, and (iii) reboiler decoupling. These scenarios are representative of realistic flexible operation of non-baseload CCS power stations. Experimental plant data was used to validate a dynamic model developed in gCCS. In the capture plant ramping scenario, increased liquid-to-gas (L/G) ratio resulted in higher CO_2 capture rate. The partial load stripping scenario demonstrated that the hot water flow directly affects reboiler temperature, which in turn, has an impact on the solvent lean loading and CO_2 capture rate. The reboiler decoupling scenario demonstrates a similar relationship. Turning off the heat supply to the reboiler leads to a gradual decline in reboiler temperature, which increases solvent lean loading and reduces CO_2 capture rate. The absorber column temperature profile is influenced by the degree of CO_2 capture. For scenarios that result in lower solvent lean loading, the absorber temperature profile shifts to higher temperature (due to the higher CO_2 capture rate).

1. Introduction

1.1. Flexible CCS

Carbon capture and sequestration (CCS) technologies are expected to play an essential role in achieving deep reductions in atmospheric CO_2 concentration for the mitigation of climate change (IPCC, 2014). To accommodate the growing use of intermittent renewable energy (*e.g.*, wind, solar), CCS will likely need to operate in a flexible manner to balance the supply of low carbon electricity (Ludig et al., 2010; van der Wijk et al., 2014; Mac Dowell and Shah, 2015; Mac Dowell and Staffell, 2016; Bandyopadhyay and Patiño-Echeverri, 2016; Mechleri et al., 2017). Flexible CCS provides additional value to the electricity system by enabling the dispatch of intermittent renewables (which have low operating costs), leading to a reduction in total system cost (Heuberger et al., 2016, 2017a,b,c). The system-wide benefits of flexible CCS are clear; however, further evaluation at a process plant scale is needed to better understand the impact of flexible operation on the performance of the CO_2 capture plant. Dynamic pilot plant studies and process modelling work will be important in assessing the feasibility of flexible operation in CO_2 capture plants (Bui et al., 2014).

Post-combustion amine-based absorption for CO_2 capture is a mature technology (Bui et al., 2018). There are a number of plants worldwide at different scale: over 37 pilot plants, 13 demonstration plants (Cousins et al., 2016) and commercial scale projects (Boundary Dam and Petra Nova). Operating experience for steady state conditions is extensive at this point. However, procedures for implementing dynamic or flexible operation strategies in pilot plants are still developing. Experience in flexible operation of pilot plants will have a vital role in understanding plant dynamics in order to improve operation strategies and control procedures. Furthermore, pilot plant experiments are essential in the development of accurate process models, and control strategies. To ensure dynamic models of CO_2 capture plants provide reliable predictions, model validation against real plant data that demonstrate transient/dynamic behaviour is required. Although there are a relatively large number of pilot and demonstration plants worldwide, openly available dynamic operating data from CO_2 capture pilot plants remain relatively limited. Fundamental models of separation processes were first developed decades ago (Treybal, 1969; Feintuch and Treybal, 1978; Krishnamurthy and Taylor, 1985a,b), these approaches were subsequently used to develop models of absorption-based CO_2 capture processes (Tontiwachwuthikul et al., 1989, 1992; Pacheco and Rochelle, 1998). Historically, the majority of process models, both steady state and dynamic, were validated using steady state pilot plant data (Kvamsdal et al., 2009; Lawal et al., 2009a,b, 2010a,b, 2012; Gáspár and Cormoş, 2011; Cormoş and Daraban, 2015; Nittaya et al.,

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2014a; Luu et al., 2015). Whilst model validation using steady state data is good, it doesn't automatically follow that this corresponds to dynamic validation. This point is demonstrated by the failure of some early attempts to describe dynamic performance, despite successful steady state validation (Kvamsdal et al., 2011; Biliyok et al., 2012). Dynamic models of CO_2 capture processes were first developed as stand-alone models of the columns. Computational advancements facilitated the development of integrated dynamic models that incorporate the capture process with the power plant. The development of dynamic CO_2 capture models was extensively reviewed in a previous contribution (Bui et al., 2014), and is therefore not extensively discussed again here. However, for completeness, we present an overview of more recent advances in the development of dynamic CO_2 capture models and pilot plant studies. The studies in the following section are summarised in Appendix A, Tables 6 and 7.

1.2. Developments in dynamic modelling and plant operation

The reliability of modelling results is questionable without verification against actual experimental data (*e.g.* lab-scale or pilot plant testing) (Bui et al., 2014). Steady state validation alone is not sufficient enough to ensure that the dynamic process model adequately describes the transient behaviour. There is key process information that only dynamic experimental data can provide, for instance, liquid residence time, plant response time and process dynamics (*i.e.*, plant response to a process disturbance). Therefore, the validation against both steady state and dynamic experimental data is necessary, in order to provide confidence in modelling results. In answer to this requirement, there is a growing number of dynamic models that have been validated against transient pilot plant data (Kvamsdal et al., 2011; Biliyok et al., 2012; Enaasen et al., 2014; Enaasen Flø et al., 2015, 2016; Garðarsdóttir et al., 2015; Wellner et al., 2016; Chinen et al., 2016; Abdul Manaf et al., 2016; Gaspar et al., 2016a; Montañés et al., 2017). The dynamic data used to validate these models vary in terms of:

- **Source of data:** from literature or dedicated dynamic pilot plant tests,
- **Type of dynamic behaviour:** *e.g.*, start-up, plant ramping,
- **Solvent type:** the majority of studies use monoethanolamine (MEA) solvent, however, some have used alternative solvents, *e.g.* AMP (Cormoş and Daraban, 2015), piperazine (Gaspar et al., 2016a),
- **Plant scale:** capacity may range between 0.3–125 tonnes CO_2 per day.

To ensure the dynamic model results are reliable for a wide range of conditions, the model ideally needs to be validated with multiple sets of dynamic data describing different types of dynamic behaviour. Models developed based on a specific pilot plant will be valid for the given pilot plant scale. Using a scale-up procedure, the validated pilot-scale dynamic model may then be used to describe a commercial scale model (Nittaya et al., 2014a,c).

Kvamsdal et al. (2011) developed a dynamic model in MATLAB®, which was subsequently used for a parametric sensitivity study on underlying model equations and alternative parameter correlations for reaction rate constant. The model was originally validated against steady state pilot plant data (for MEA solvent) from the Separation Research Program (SRP) at the University of Texas at Austin (Kvamsdal et al., 2009). The SRP pilot plant is designed to capture 200–250 kg_{CO_2}/h (4.8–6.0 tonne CO_2/day). Dynamic model validation was conducted using pilot plant datasets from dedicated dynamic tests at the validation of CO_2 capture (VOCC) pilot plant at NTNU/SINTEF. This plant was smaller than the SRP plant with a capture capacity of 50–70 kg_{CO_2}/h (1.2–1.8 tonne CO_2/day). Biliyok et al. (2012) also used both steady state and dynamic data from the SRP pilot plant to validate a dynamic MEA-based model in gPROMS®.

Enaasen Flø et al. (2015) developed a dynamic model of an MEA-based CO_2 capture process in MATLAB®. Steady state and dynamic data from the Gløshaugen pilot plant (Pinto et al., 2014) was used for model validation under both steady state and dynamic conditions. This plant produces up to 12.5 kg_{CO_2}/h (0.3 tonne CO_2/day) when operating with MEA solvent (Pinto et al., 2014), thus is much smaller in scale compared to the SRP and VOCC pilot plants.

The importance of having an appropriate control strategy was highlighted in a study by Garðarsdóttir et al. (2015). This work evaluated the impact of dynamic operation on an integrated system comprising of a coal-fired power plant with CO_2 capture. The MEA-based absorption process was modelled using Modelica® modelling language and simulated using Dymola (Prölß et al., 2011; Åkesson et al., 2012). This model was validated against both steady state and dynamic data from the Esbjerg pilot plant located at the Dong Energy coal-fired power station in Denmark (captures 1 tonne CO_2/h, Faber et al., 2011). A steady state model describing the performance of the Nordjyllandsværket power plant (thermal efficiency of $47\%_{LHV}$, International Energy Agency, 2007) with a capture system integrated in the steam cycle was developed in Ebsilon 7.0 (Garðarsdóttir et al., 2015).The implementation of an active control strategy in the integrated system improved the capture plant performance by reducing heating requirements, and improving capture efficiency and response time. The amount of liquid in the system had a significant impact on the process dynamics. A system with a larger volume of liquid had a slower response, and therefore reduced the transition speed between different load conditions (Garðarsdóttir et al., 2015).

Wellner et al. (2016) also analysed the dynamics of an integrated system, *i.e.*, a coal-fired power plant with post-combustion CO_2 capture plant. The dynamic model was developed using modelling language Modelica®. The CO_2 capture process was first validated using steady state and dynamic data from pilot plant Heilbronn, which captures 300 kg_{CO_2}/h (7.2 tonnes CO_2/day) at a capture rate of 90% (Rieder and Unterberger, 2013). Subsequently, the capture process was coupled with the model of the coal-fired power plant. The modelling results demonstrated that an increase in power plant generation could be achieved through a 50% reduction in steam extraction for the CO_2 capture process. Potentially, this interaction between power plant and capture plant could provide a means for primary frequency control power/electricity. The reboiler valve was shown to be a good variable for providing fast and reliable control power (Wellner et al., 2016). Models such as these are essential for performance optimisation of the integrated system as they account for the coupling effects associated with linking the CO_2 capture process with the power plant.

Chinen et al. (2016) developed a process model of an MEA-based CO_2 capture plant; the focus was to establish a robust reference model for a large operating range. In additional to validating the dynamic response of the model, the physical property models were also validated in detail to ensure property estimates were satisfactory over the entire range of operating conditions. The model was developed using a combination of AspenTech software—the steady state model in Aspen Plus® and dynamic model in Aspen Plus Dynamics®. Submodels (*e.g.*, physical property models, thermodynamic framework) are defined as a

FORTRAN user model and integrated into Aspen. The experimental data used to validate this mode was sourced from a pilot plant at the National Carbon Capture Centre (NCCC) in Alabama (Chinen et al., 2016). The reported capture capacity of the facility ranges between ~80–800 kg_{CO_2}/h (Cousins et al., 2016).

Instead of the first principles modelling approach, Abdul Manaf et al. (2016) developed a "mathematical black box" model to evaluate the dynamics of an MEA-based CO_2 capture pilot plant. The black box approach employs a multi-variable non-linear autoregressive with exogenous input (NLARX) model, which characterises the CO_2 capture plant as a multiple input, multiple output and non-linear process. Dynamic data from the Tarong pilot plant (capture capacity of 100 kg_{CO_2}/h, Cousins et al., 2012) was used to develop data driven models of each unit operation. The individual unit models were integrated to generate various process configurations and controllability analysed (Abdul Manaf et al., 2016). The limitation of using a data-driven model is that the outcomes of this work are based on specific operating conditions (*i.e.*, valid within the operating range of the plant data). Using plant data from a sufficiently large number of operation scenarios and wide operating range will ensure that data-driven models have reasonable accuracy.

Gaspar et al. (2016a) evaluated the controllability and flexibility of CO_2 capture processes for two solvent systems, piperazine and MEA. It was possible to validate the MEA-based model against steady state and dynamic pilot plant data. However, only steady state pilot plant data was available for the validation of the piperazine model (Gaspar et al., 2015, 2016b,c). This work provided valuable insight into the dynamics of two different solvent systems. It was found that the piperazine plant had a longer settling time compared to the MEA system. Also, the piperazine plant was able to reject the disturbances faster[1] and with less variability in the power plant load. The differences in physical properties of the two amines affect the mass transfer and hydraulic characteristics, which in turn impacts the process dynamics. A proposed proportional integral (PI) based control structure was evaluated. The presence of constraints in the availability of steam reduces performance of both MEA and piperazine controller systems; driving the MEA plant towards drying out/flooding and reducing CO_2 capture performance in the piperazine plant. This suggests a need for advanced control structures (*e.g.*, Model Predictive Control) which can account for operating limits/constraints of the process parameters (*e.g.*, limited steam availability) (Gaspar et al., 2016a). Improving the controllability could improve the disturbance rejection capacity of the system (*i.e.*, minimal drift from the nominal operating point) (Skogestad and Wolff, 1996). The plant operability in this study was dependant on the physical properties of the solvent (*i.e., solvent type*) and process constraints (*e.g.*, steam availability), which consequently dictates system controllability (best control structure for the given process).

The development of dynamic models using data from relatively larger capture plants has recently been published. The Brindisi pilot plant in Italy can capture between 1000–2500 kg_{CO_2}/h (40–60 tonnes CO_2/day) from a coal-fired power plant, where the design capacity is 2000 kg_{CO_2}/h (Enaasen Flø et al., 2016; Mangiaracina et al., 2014). Enaasen Flø et al. (2016) developed a dynamic model of the Brindisi pilot plant in a process simulation software called K-Spice® (Enaasen et al., 2014; Enaasen Flø et al., 2016) and validated against dynamic plant data (presented in Enaasen et al., 2014). This validated model was subsequently used to evaluate the performance of several flexible operation strategies. Simulation of load following showed that the capture plant had a fast response upon changes to load. Due to the constraint requiring an average capture rate of 90%, the exhaust gas venting and varying steam supply strategies were very limited in terms of flexibility. The solvent storage improved plant flexibility the most (compared to other scenarios), however, investment costs would be significant (Enaasen Flø et al., 2016).

The Technology Centre Mongstad (TCM) CO_2 capture plant, considered demonstration scale (Cousins et al., 2016), can operate in two configuration modes: (i) combined heat and power (CHP) operation with a capture capacity of 80 tonnes CO_2/day and flue gas CO_2 concentration of 3.5 vol%; and (ii) refinery catalytic cracker (RCC) operation with a capture capacity of 275 tonnes CO_2/day and flue gas CO_2 concentration of 13–14 vol% (Montañés et al., 2017; Hamborg et al., 2015). Using the modelling language Modelica®, Montañés et al. (2017) developed a dynamic model of the TCM plant operating in the CHP configuration with MEA solvent. The model was successfully validated against both steady state and dynamic plant data from TCM. The dynamic response of main process parameters to step changes was found to be slower at lower operating load. Also, the performance of several control structures during transient operation was evaluated. The best performing strategies involved the manipulation of reboiler duty to control CO_2 capture rate and rich solvent flow to control the stripper bottom temperature (Montañés et al., 2017).

One key challenge is to ensure pilot plant datasets have enough detail to enable an adequate description of the process in the dynamic model. Most pilot plants are equipped with similar measurement and monitoring instrumentation, also chemical analysis techniques across different pilot plants are relatively consistent (*e.g.*, automatic/manual titration). In the case where pilot plant conditions are dynamic, the ability to monitor transient behaviour in the liquid phase is essential (Bui et al., 2016a,b; Tait et al., 2016). However, most pilot plants are not equipped for online chemical analysis of the liquid solvent. Only a few pilot plants are able to provide dynamic data for online CO_2 loading and solvent composition (Bui et al., 2016b). Some pilot plant studies are beginning to specifically investigate dynamic and flexible operation of CO_2 capture (Mangiaracina et al., 2014; Bui et al., 2016a; Tait et al., 2016, 2018; de Koeijer et al., 2018; Monta nés et al., 2018)—these pilot plants have a system in place for online measurement of CO_2 concentration. Evaluating plant performance during dynamic operation will be essential in understanding the limitations of plant flexibility, *e.g.*, constraints with process parameter operating ranges, ramping capabilities.

It is important to recognise that discrepancies between the model predictions and pilot plant data can be attributed to errors in both the model and experimental results. Early work in evaluating flexible operation of CO_2 capture demonstrates that deviation between the model and data may be attributed to multiple factors, for example, insufficient experimental data, lack of process information, incorrect experimental measurements, poorly described physical properties, or combination of these. Proactive collaboration between experimentalists and modellers can help reduce the introduction of error and manage uncertainty. Typically, the modelling approach has been to first develop a process model, and then subsequently validate this model with experimental data close at hand. In some instances, the models are not validated with experimental data, and instead, validated against models developed in alternative software (Bui et al., 2014). Due to the limited availability of pilot plant data, particularly dynamic data, process modellers suffer from a paucity of choice of datasets for dynamic model validation. Consequently, dynamic dataset selection is based on availability rather than quality or suitability. Process modellers may only have access to data from small-scale pilot plants, or process data for a small operating range. Thus far, only two dynamic models have been validated against dynamic data from demonstration-scale CO_2 capture plants, the Brindisi plant (Enaasen et al., 2014; Enaasen Flø et al., 2016), and the TCM facility (Montañés et al., 2017). For efficient use of experimental resources, laboratory experimentalists, pilot plant operators, process modellers, and process control designers should communicate more effectively, enabling the alignment of research objectives. This will help

[1] Disturbance rejection is ability to return to the desired set-point conditions after deviation due to a disturbance (Dinh et al., 2012; Skogestad, 2004). Processes with more controllability tend to have better disturbance rejection capacity (Skogestad and Wolff, 1996).

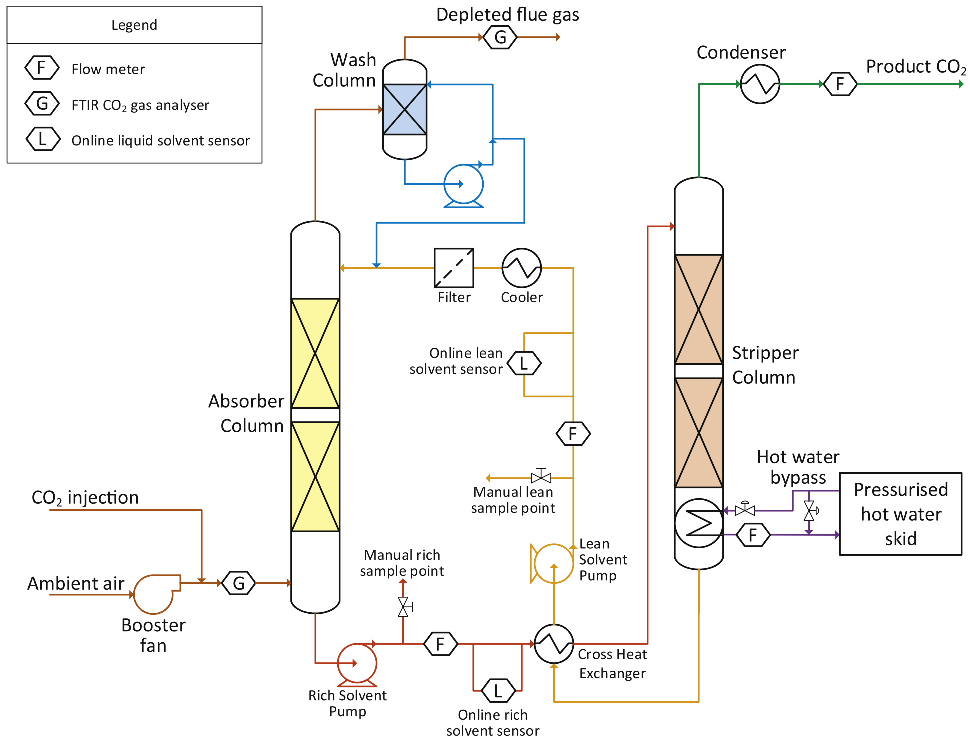

Fig. 1. Process overview of the UKCCSRC PACT CO_2 capture pilot plant.

Table 1
Specifications of the UKCCSRC PACT CO_2 capture pilot plant.

Specification	Water wash	Absorber	Stripper
Geometry	Cylindrical	Cylindrical	Cylindrical
Packing type	Intalox IMTP 25 (random)	Sulzer Mellapak CC3 (structured)	Intalox IMTP 25 (random)
Packing height (m)	1.2	6.5	6.1
Diameter (m)	0.30	0.30	0.30
Cross sectional area (m^2)	0.071	0.071	0.071
Material of packing	Metal	Metal	Metal
Sump volume (L)	–	70	400
Pressure	Atmospheric	Atmospheric	120–300 kPa abs

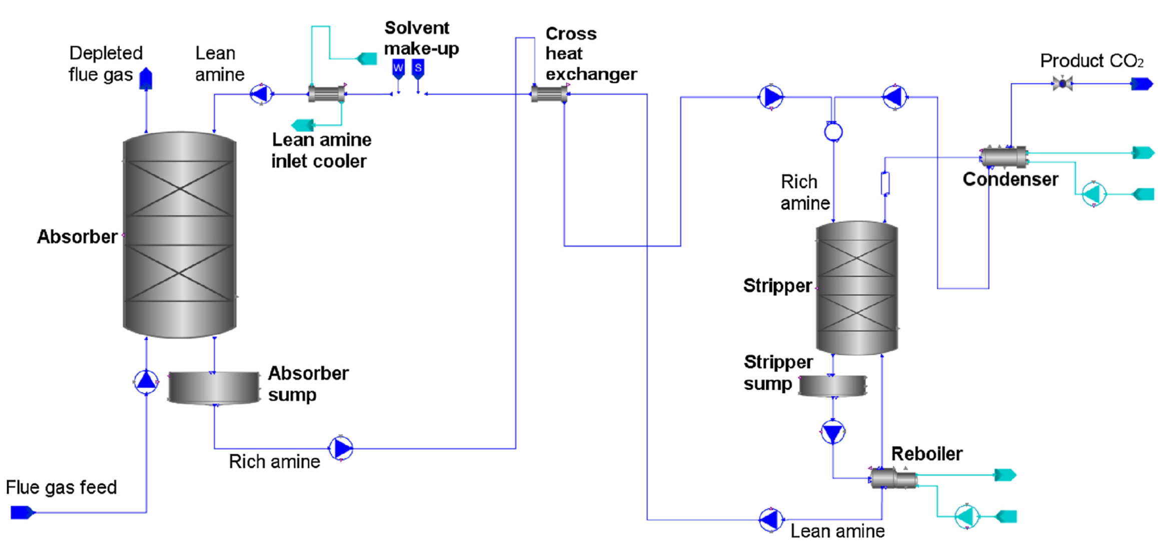

Fig. 2. Model of the UKCCSRC PACT CO_2 capture pilot plant in gCCS.

Table 2
Key process parameters for steady state case A and case B, data from the August 2016 test campaign at the UKCCSRC PACT pilot plant.

Specification	Case A	Case B
Flue gas flow rate (Nm^3/h)	199.2	199.4
Feed flue gas CO_2 concentration (vol%)	12.3	12.0
Lean solvent flow (kg/h)	974.3	1181.7
L/G ratio (kg liq/Nm^3 gas)	4.89	5.93
Absorber solvent inlet temperature (°C)	40.2	40.1
Absorber flue gas inlet temperature (°C)	45.2	45.9
Stripper solvent inlet temperature (°C)	100.5	97.7
Stripper pressure (kPa abs)	147	151
Reboiler temperature (°C)	118.1	116.3
Lean CO_2 loading (mol CO_2/mol MEA)	0.1290	0.2359
Rich CO_2 loading (mol CO_2/mol MEA)	0.3700	0.4115
PACT plant CO_2 capture rate (%)	91.2	86.8
gCCS model CO_2 capture rate (%)	89.5	83.9
Percentage difference CO_2 capture rate (%)	1.9	3.3

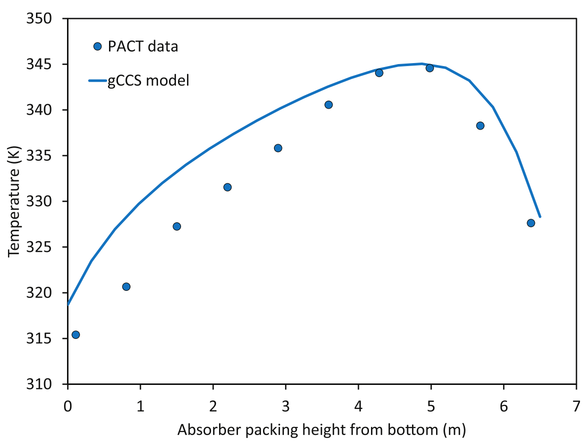

Fig. 3. Steady state validation of the gCCS model against Case A plant data. Average absolute deviation between the PACT data and gCCS predictions for absorber temperature is 3.8 K (calculated in Table 11, Appendix C).

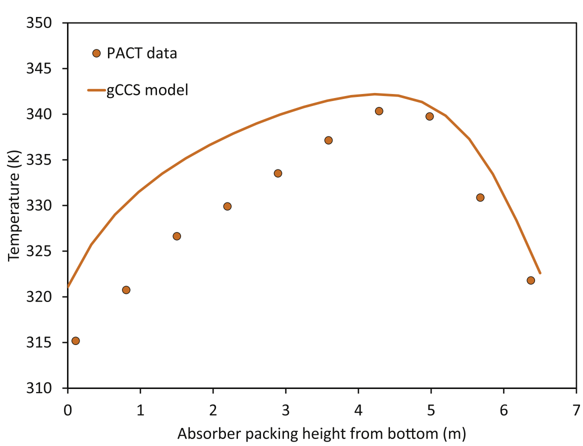

Fig. 4. Steady state validation of the gCCS model against Case B plant data. Average absolute deviation between the PACT data and gCCS predictions for absorber temperature is 5.4 K (calculated in Table 11, Appendix C).

produce pilot plant studies that can serve multiple purposes—experimental investigation and process modelling.

1.3. Study objectives

The aim of this work is to evaluate the performance of a CO_2 capture plant during dynamic operation through a combination of pilot plant experiments and dynamic model simulations. A dynamic operation campaign was conducted at the UKCCSRC PACT pilot plant using 30 wt % monoethanolamine (MEA) solvent (Tait et al., 2018). A dynamic model of this pilot plant is validated and used to model different dynamic operation scenarios. The dynamic operation campaign investigated seven dynamic operation scenarios, presented in Tait et al. (2018). These scenarios are representative of potential flexible operation of CCS coal-fired power stations in future electricity systems, using recent insights into their role as energy and flexibility service providers (Bruce et al., 2016). They impose realistic ramp rates comparable to coal-fired boilers and the extraction of superheated steam from steam turbine power cycles. Three dynamic datasets were selectively chosen for model validation: (i) partial load stripping, (ii) capture plant ramping, and (iii) reboiler decoupling. These dynamic datasets were selected as they represented scenarios that consider the effects of integration on CO_2 capture performance, *i.e.* operating the CO_2 capture plant in accordance to requirements of power generation (described in Section 4.2).

This is the first dynamic model of the UKCCSRC PACT CO_2 capture pilot plant. Previous contributions only modelled the PACT capture plant under steady state conditions using Aspen Plus (Rezazadeh et al., 2016) and Aspen HYSYS (Akram et al., 2016). The selection of scenarios from Tait et al. (2018) and the development of this dynamic model involved close collaboration with the pilot plant operators, using their insights to ensure the process is accurately modelled. The dynamic analysis will investigate how key process parameters interact to generate a dynamic response in a CO_2 capture plant. Understanding the dynamic interaction between key process parameters will be essential in the development of robust control strategies for flexible operation in CO_2 capture plants. Previous studies have observed that process plant dynamics (*e.g.*, plant response time, liquid residence time, stabilisation time) are closely related to the total capacity of liquid volume (Garðarsdóttir et al., 2015; Bui et al., 2016a; Tait et al., 2016). The evaluation of dynamic test results from many different pilot plants can help elucidate the fundamental relationship between plant scale and plant dynamics. The detailed dynamic pilot plant datasets (provided in Appendix B) are an important contribution to the future study of CO_2 capture plant dynamics.

The remainder of the paper is structured as follows: (i) First the experimental testing conducted at the UKCCSRC PACT pilot plant is described. (ii) An outline of the dynamic model is provided. (iii) The model simulation and validation results are presented and discussed. Lastly, (iii) the paper concludes with a discussion of the future research directions for the flexible operation of CO_2 capture plants.

2. Experimental testing: UKCCSRC PACT CO_2 capture pilot plant

The dynamic operation test campaign was conducted during August 2016 at the Pilot-scale Advanced Capture Technology (PACT) facility of the UK Carbon Capture and Storage Research Centre (UKCCSRC). The PACT pilot plant (shown in Fig. 1) has a CO_2 capture capacity of 1 tonne

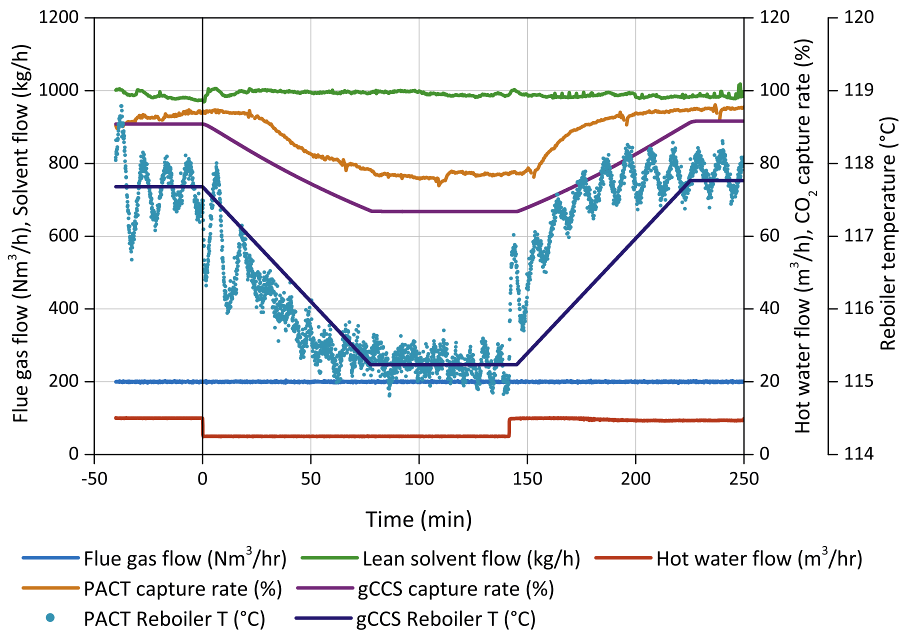

Fig. 5. Process parameter measurements during the partial load stripping scenario. At time 0 min, the hot water supply to the reboiler is decreased from 10 m^3/h to 5 m^3/h, it is then increased back to 10 m^3/h at 142 min.

of CO_2 per day at a capture rate of > 85% using 30 wt% monoethanoloamine (MEA) aqueous solution. The plant is designed to process flue gas from different sources, including a gas turbine, a coal/biomass burner or synthetic flue gas from a gas mixing skid (composition in Table 9, Appendix B). In this test campaign, the feed synthetic flue gas was a mixture of ambient air and CO_2 from the gas mixing skid.

The PACT pilot plant has a conventional design consisting of a packed absorber column, packed water wash column, and packed stripper column. Design specifications of the columns (water wash absorber and stripper) are shown in Table 1 and packing specification available in Table 8. A booster fan is used to increase the pressure of the flue gas at the absorber column inlet. In the absorber, lean solvent entering from the top is counter-currently flowed with the flue gas, resulting in the absorption of CO_2 from the flue gas. The processed flue gas exits the top of the absorber column and passes through the water wash column, reducing solvent entrainment (minimises solvent loss). The rich solvent exiting the bottom of the absorber is heated in the cross heat exchanger before entering the stripper column. Pressurised hot water at a temperature of between 120–125 °C supplies heat to the reboiler for solvent regeneration. As the rich solvent flows down the stripper column, the desorption of CO_2 from the solvent produces a CO_2 product stream, which passes through an air-cooled condenser and reflux drum (removes entrained droplets). Lean amine exiting the stripper is cooled in the cross heat exchanger and further cooled by an air cooler (controls liquid temperature at absorber inlet). Subsequently, the lean amine passes through a carbon filter to remove any degradation products.

The objective of this August 2016 test campaign was to implement various dynamic scenarios including realistic start-up and shut-down operations, capture bypass operations, and observe the effect on critical plant parameters. Another component of this experimental work was to evaluate the performance of the online solvent sensing device, developed in-house at The University of Edinburgh (Tait et al., 2016, 2017, 2018). The device uses *in situ* measurements of physical properties to determine the CO_2 loading and amine concentration of the solvent, providing real-time measurements of solvent composition (Tait et al., 2016).

Fig. 1 indicates the points in the process where stream flow rate and composition are measured. Flow rate of both the lean and rich streams are measured with a Coriolis flow meter. Rich and lean solvent is collected from the manual sample points at specific times. Chemical analysis of these samples provides the solvent composition. In addition to the manual liquid analysis, online rich and lean solvent sensors were installed to gather instantaneous measurements of CO_2 loading (essential for this dynamic test campaign). Differential pressure is measured across the packed bed and temperature is measured along the height of the absorber column to produce a temperature profile. The measurement of absorber column temperature profile is a crucial measurement for model development. During dynamic operation of the plant, the change in process parameters (*i.e.* flue gas flow, solvent flow) will have an impact on the CO_2 absorption performance. Dynamic behaviour can be observed in the plant through observing changes in the absorber column temperature profile. Further information on this dynamic test campaign is published by Tait et al. (2018).

3. Dynamic model description

The model of the UKCCSRC PACT CO_2 capture plant was developed in gCCS (PSE, 2018), a software specifically designed for modelling CCS systems. A flowsheet of a CO_2 capture process was developed based on specifications of the UKCCSRC PACT CO_2 capture plant. The model can operate under both steady state and dynamic conditions. The rate-based

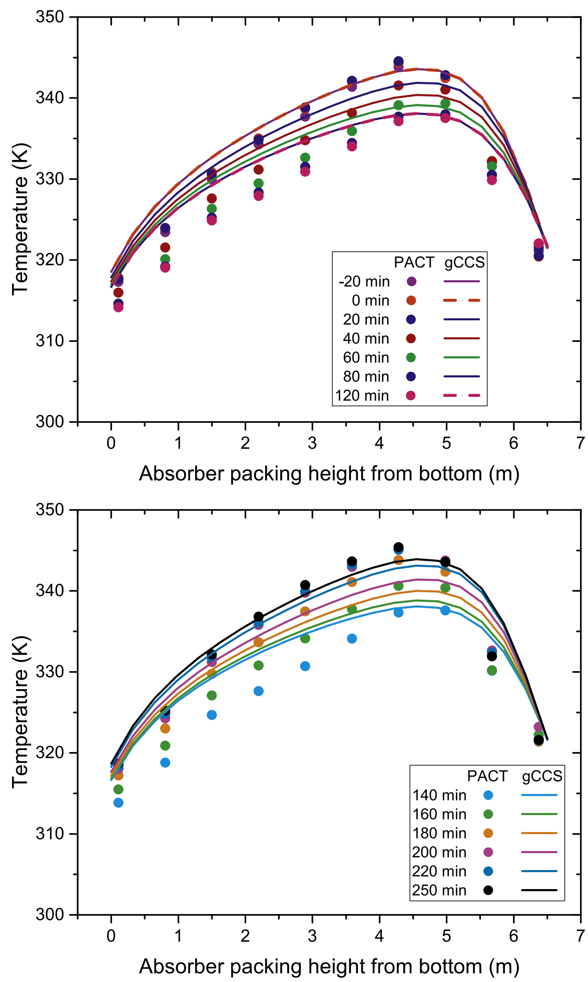

Fig. 6. Dynamic validation of the gCCS modelled absorber temperature against plant data for the partial load stripping scenario. To prevent the overlapping of absorber temperature profiles, the data is separated into (top) time −20 min to 120 min, and (bottom) time 140 min to 250 min. Average absolute deviation between the PACT data and gCCS predictions for absorber temperature ranges between 2.0 and 3.3 K (calculated in Table 13, Appendix C).

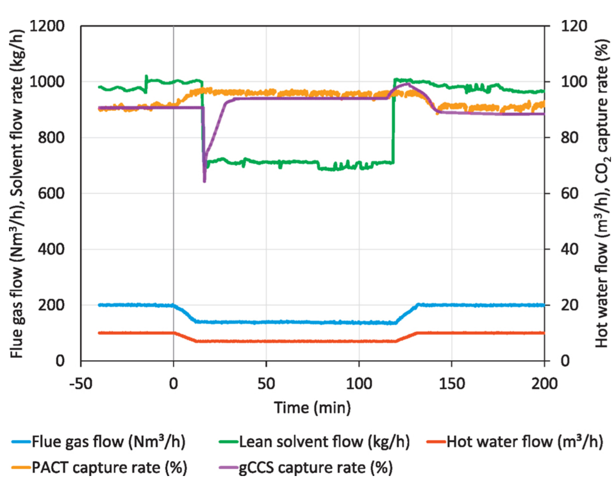

Fig. 7. Process parameter measurements during the capture plant ramping scenario. At time 0 min, the flue gas, solvent and hot water flows are decreased simultaneously, before increasing simultaneously at 120 min.

absorber and stripper column models use the Billet correlation (Billet and Schultes, 1993) for the mass transfer model (suitable for both structured and random packing).

The thermophysical properties of the process fluids are described with the gSAFT physical properties package, which is the implementation of the statistical associating fluid theory (SAFT) (Chapman et al., 1989, 1990) for process modelling and simulation. The two equations of state available in gSAFT are: (i) SAFT-VR Square Well (SAFT-VR SW), SAFT method for variable-range potentials (Gil-Villegas et al., 1997; Galindo et al., 1998); and (ii) SAFT-γ Mie, a group contribution method (Lafitte et al., 2013; Papaioannou et al., 2014). gSAFT is used to specifically describe the thermodynamics and fluid-phase equilibria for the chemisorption of CO_2 in amine solvents. Detailed information on the development of the molecular models has been provided by Mac Dowell et al. (2010, 2011) and Rodriguez et al. (2012). Furthermore, how these models are integrated into process models has also been detailed (Mac Dowell and Shah, 2015, 2013; Mac Dowell et al., 2013). Fig. 2 illustrates the dynamic model flowsheet in gCCS based on the configuration of the UKCCSRC PACT CO_2 capture plant (described in Section 2).

The PACT pilot plant equipment information and feed stream conditions used as model input specifications are presented in Appendix A, including column dimensions and packing specifications. To ensure that the process dynamics are accurately described, it is important to include column sump volume and equipment capacity as model inputs. The detailed datasets for the steady state and dynamic scenarios are presented in Appendix B, where key model input specifications include composition, flow rate and temperature of the feed streams (*i.e.*, flue gas and lean solvent). The following section presents the model simulation procedure and validation results for steady state (Section 4.1) and dynamic (Section 4.2) scenarios.

Uncertainty in both the experimental data and model can have an impact on the model validation results. Experimental data values have an error or uncertainty associated with the precision of the instrument or technique. Thus, the use of experimental measurements as input specifications for a model potentially introduces uncertainty in the modelling results. The titration measurements of solvent lean CO_2 loading was used as a model input and has an uncertainty of ± 3.15% relative (Tait et al., 2018). During steady state operation of the PACT pilot plant, small fluctuations in plant measurements can be observed. In Figs. 5 and 10, there are small variations in CO_2 capture rate during the period of initial conditions (before 0 min). In contrast, the model assumes ideal steady state, where process parameters remain constant. The non-ideal nature of the experimental data is a source of uncertainty, which can contribute to the deviation in model validation. The quantification of uncertainty was not the focus of this study. However, the evaluation of uncertainty could potentially be included in future research on dynamic modelling of CO_2 capture plants.

4. Dynamic model simulation and validation

4.1. Steady state model validation

Process conditions for two steady state datasets from the PACT pilot plant are given in Table 2. These steady state cases were chosen as each represents operation at different liquid-to-gas (L/G) ratios and reboiler temperatures. The dynamic model was configured to simulate these steady state scenarios. Figs. 3 and 4 shows that the model predictions for absorber temperature profile are in agreement with the PACT plant data. Furthermore, the dynamic model accurately predicts the position of the temperature bulge along the height of the absorber (in both case A and B), which is indicative of a robust description of the underlying

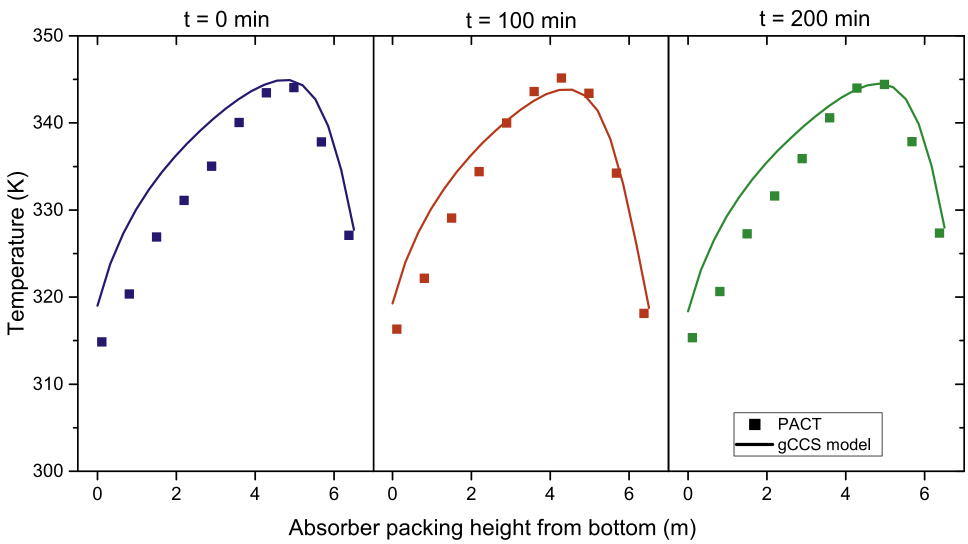

Fig. 8. Dynamic validation of the gCCS modelled absorber temperature against plant data for the capture plant ramping scenario. Average absolute deviation between the PACT data and gCCS predictions for absorber temperature ranges between 2.7 and 4.3 K (calculated in Table 14, Appendix C).

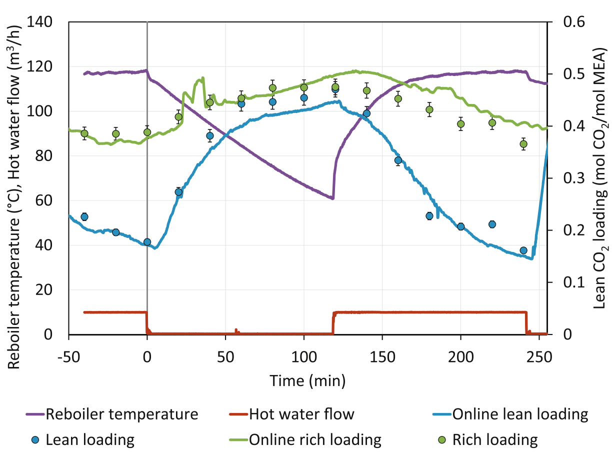

Fig. 9. Effect of hot water flow on reboiler temperature and CO_2 loading during the reboiler decoupling scenario. Hot water to the reboiler is turned off at time 0 min and then restored to 9.9 m^3/h at time 118 min. The ± 3.15% relative uncertainty of solvent loading titration measurements are shown by error bars.

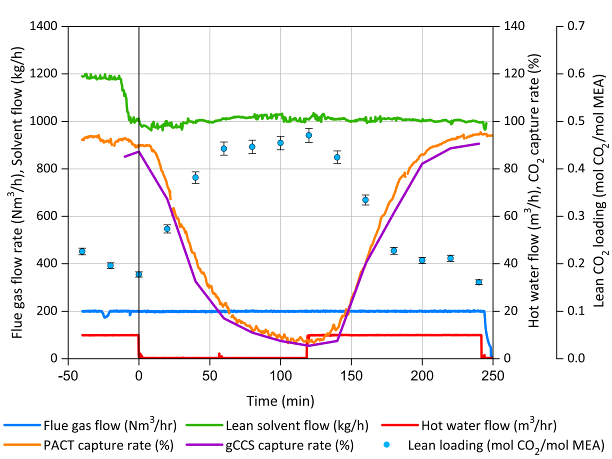

Fig. 10. Process parameter measurements during the reboiler decoupling scenario. At time 0 min, the heat supply to the reboiler is turned off and then restored to 9.9 m^3/h at time 118 min. The ± 3.15% relative uncertainty of solvent loading titration measurements are shown by error bars.

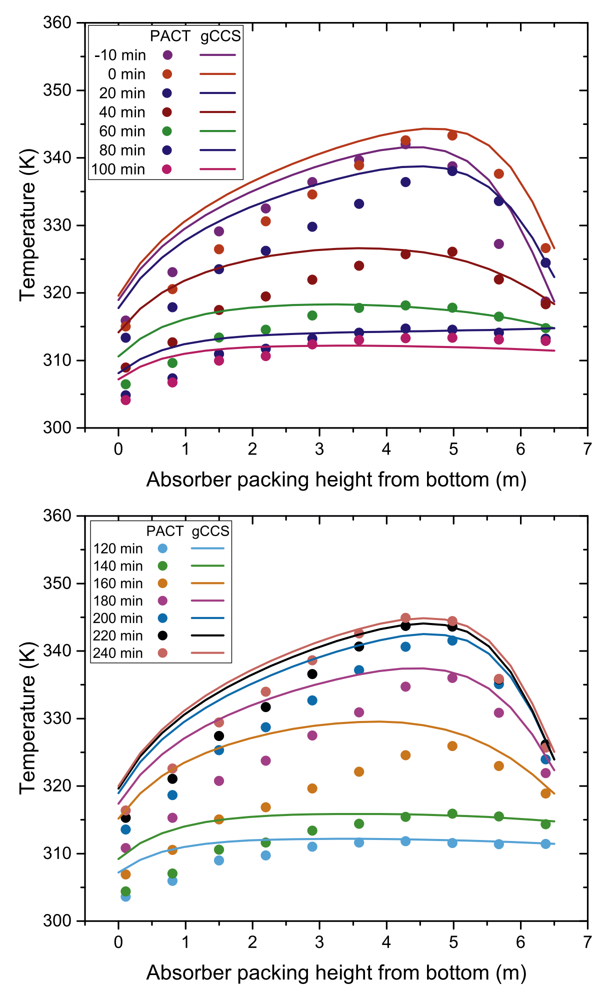

Fig. 11. Dynamic validation of the gCCS modelled absorber temperature against plant data for the reboiler decoupling scenario. To prevent the overlapping of absorber temperature profiles, the data is separated into (top) time −10 min to 100 min, and (bottom) time 120 min to 240 min. Average absolute deviation between the PACT data and gCCS predictions for absorber temperature ranges between 1.6 and 7.0 K (calculated in Table 16, Appendix C).

Table 3
Partial load stripping model predictions compared with plant results.

Time (min)	0	140	250
Hot water flow rate (m^3/h)	10.0	5.0	10.0
Reboiler temperature (°C)	117.4	114.9	118.1
Lean CO_2 loading (mol CO_2/mol MEA)	0.1741	0.2781	0.1632
Rich CO_2 loading (mol CO_2/mol MEA)	0.3688	0.4164	0.3501
PACT plant CO_2 capture rate (%)	93.7	77.3	95.5
gCCS model CO_2 capture rate (%)	90.8	66.8	91.7
Difference	2.9	10.5	3.9
Percentage difference capture rate (%)	3.1	13.6	4.0

Table 4
Capture plant ramping model predictions compared with plant results.

Time (min)	0	100	200
Flue gas flow rate (Nm^3/h)	198.7	137.7	199.5
Lean solvent flow rate (kg/h)	999.9	706.9	974.4
L/G ratio (kg liq/Nm^3 gas)	5.03	5.13	4.88
Hot water flow rate (m^3/h)	10.0	7.0	10.0
Reboiler temperature (°C)	117.7	117.9	118.1
Lean CO_2 loading (mol CO_2/mol MEA)	0.1322	0.1211	0.1286
Rich CO_2 loading (mol CO_2/mol MEA)	0.3995	0.3508	0.3639
PACT plant CO_2 capture rate (%)	91.0	95.1	90.0
gCCS model CO_2 capture rate (%)	90.7	94.0	88.4
Difference	0.3	1.1	1.6
Percentage difference CO_2 capture rate (%)	0.33	1.2	1.8

Table 5
Reboiler decoupling model predictions compared with plant results.

Time (min)	−10	0	60	120	180	240
Hot water flow rate (m^3/h)	9.9	1.3	0.29	9.4	10.0	10.0
Reboiler temperature (°C)	117.4	117.6	84.6	74.7	115.6	117.5
Lean CO_2 loading (mol CO_2/mol MEA)	0.2259	0.1775	0.4427	0.4706	0.2274	0.1613
PACT CO_2 capture rate (%)	92.3	89.9	22.6	7.6	71.8	95.0
gCCS CO_2 capture rate (%)	85.1	87.2	17.0	5.5	61.5	90.6
Difference	7.2	2.7	5.6	2.1	10.3	4.3
Percentage difference (%)	7.8	3.0	24.9	28.1	14.3	4.6

physics of this system. The average absolute percentage deviation (average APD) for model predictions of absorber temperature for case A and case B is 1.2% and 1.6%, respectively (*i.e.*, case A temperature prediction is slightly more accurate than case B). The CO_2 capture rate is also reliably predicted by the model, where percentage difference is 1.9–3.3% (Table 2).

In comparing the two steady state cases, Case A has a higher temperature profile compared to Case B (Figs. 3 and 4). Although Case A has a lower L/G ratio than Case B, the reboiler temperature of Case A is greater (118.1 °C compared to 116.3 °C). In comparison with Case B, the increased reboiler temperature of Case A results in lower solvent lean loading, which in turn, increases CO_2 capture rate and absorber temperature (shown in Table 10 of Appendix C). The shape of the absorber profile and location of the temperature bulge depends on several factors: L/G ratio, solvent properties (*e.g.*, heat of absorption), packing height, and flue gas CO_2 concentration (Kvamsdal and Rochelle, 2008). The location of the temperature bulge typically shifts closer to the base of the absorber with increased L/G ratio, decreased packing height, or lower flue gas CO_2 concentration (Kvamsdal and Rochelle, 2008). The higher L/G ratio of case B compared to case A (both have similar flue gas CO_2 concentration) shifts the temperature bulge closer to the base (case A is 4.9 m from the base, whereas case B is 4.2 m). In both cases, the gCCS model over-predicts absorber temperature, with the greatest discrepancy occurring at the base of the column. Along the height of the column, the flue gas entering at the base has the highest CO_2 concentration, whereas the solvent at the base is rich and has high CO_2 loading. The model appears to over-predict the degree of CO_2 absorption occurring at the base of the column. Consequently, the temperature of the rich solvent exiting the absorber is overestimated by 5–7 K. To mitigate potential downstream errors (*e.g.*, stripper performance), the outlet temperature of the rich solvent stream in the cross heat exchanger is specified as a model input using plant data.

4.2. Dynamic operation of the capture plant

Three dynamic operation scenarios are presented in this paper:

1. **Partial load stripping:** decreases heat supply to the reboiler (*e.g.* if the power plant steam cycle requires more steam, the amount extracted may be reduced).
2. **Capture plant ramping:** simultaneously decreases/increases the flow rates of flue gas, solvent and hot water, investigates the effect of load following through plant ramping on overall CO_2 capture performance.
3. **Reboiler decoupling:** the heat supply to the reboiler is turned off (*e.g.* power plant needs to operate at full generation capacity), after a period of time, reboiler heat supply is restored.

Further detailed descriptions of each scenario and the dynamic model validation results are presented below. For each dynamic operation scenarios, steady state initial conditions were first established. The period of initial conditions corresponds to the negative values of time in Figs. 5, 7, 10 and 9 (*i.e.*, time before 0 min). At 0 min, a process disturbance is implemented and dynamic behaviour observed (positive values of time). The temperature profile for time = 0 min in Figs. 6, 8 and 11 represents the initial conditions just before introduction of the process disturbance. The data for capture rate has discontinuities (missing measurement points) at times that purging of the outlet FTIR gas analysers occurs (duration of minutes).

4.2.1. Partial load stripping

This scenario demonstrates the effect of step-changes to the hot water flow rate whilst maintaining constant flue gas flow and solvent flow rate. The PACT plant initially operates at a hot water flow rate of 10 m^3/h, which translates to a reboiler temperature of 117.4 °C and CO_2 capture rate of 93.7% (Fig. 5 and Table 12). At time = 0 min, the hot water flow rate is reduced to 5 m^3/h, decreasing the reboiler temperature to 114.9 °C. The lean CO_2 loading subsequently increased to 0.278 mol CO_2/mol MEA (Table 3) and CO_2 capture rate decreased to 77.3%. At 142 min, the hot water flow rate is increased back to 10 m^3/h, increasing the reboiler temperature to 118.1 °C. This led to a decrease in lean CO_2 loading to 0.163 mol CO_2/mol MEA, resulting in a higher CO_2 capture rate of 95.5%.

The dynamic model of the PACT plant was used to simulate the partial load stripping scenario. Fig. 6 demonstrates that there is good agreement between the predicted absorber temperature profile and the experimental data from the PACT plant. The position of the temperature bulge along the height of the absorber has been accurately predicted. Similarly, the CO_2 capture rate is reasonably predicted, with a difference varying between 1.2–14.9%, shown in Fig. 5 (and in Appendix C, Table 13). The model assumes that the reboiler temperature increases and decreases linearly (Fig. 5). However, the dynamic changes in pilot plant reboiler temperature is non-ideal and fluctuates. In Fig. 5 from 142 min onwards, the divergence in reboiler temperature between the model and pilot plant increases during the dynamic phase (*i.e.*, 142 to 200 min). Consequently, the divergence between pilot plant data and model predictions of CO_2 capture rate also increases over the period of 142–200 min. The predicted absorber temperature is within an average accuracy of 2.0–3.3 K of the pilot plant measurements, where average APD is 0.7–1.0% (Table 13, Appendix C). Overall, there is good agreement between the predicted dynamic trends and the actual pilot plant behaviour.

The partial load stripping scenario demonstrates the direct effect of hot water flow rate on the reboiler temperature, which in turn, has an impact on the lean CO_2 loading and CO_2 capture rate. For higher hot water flow rate, the reboiler temperature increases, lowering the lean CO_2 loading, increasing CO_2 capture rate, and a higher absorber temperature profile is observed.

4.2.2. Capture plant ramping

The process parameters adjusted during the capture plant ramping scenario include the flue gas flow rate, hot water flow and solvent flow rate. As shown in Fig. 7, the flue gas flow and hot water flow were ramped simultaneously (*i.e.*, incrementally increased/decreased over time), whereas the solvent flow rate was adjusted to the set-point value as one step-change. Table 4 shows that the reboiler temperature was relatively constant for the three time periods. This indicates that the magnitude of the changes to hot water flow rate was not significantly large enough to have an effect on reboiler temperature, thus the effect on the CO_2 capture rate may be negligible. The flue gas flow and solvent flow were ramped at different proportions (0 min and then at 120 min), subsequently resulting in varied L/G ratio during the scenario. An increase in L/G ratio resulted in a higher CO_2 capture rate (Table 4), which concurs with earlier pilot plant and modelling work (Artanto et al., 2012, 2014; Krótki et al., 2016; van de Haar et al., 2017). Conversely, reducing the L/G ratio decreased the CO_2 capture rate.

For the capture plant ramping scenario, the dynamic model predicts the absorber temperature profile and location of the temperature bulge accurately (Fig. 8). The accuracy of model predictions for absorber temperature are within an average of 2.7–4.3 K deviation from the PACT pilot plant data (average APD of 0.83–1.3%), as shown in Table 14, Appendix C. Fig. 7 shows that as lean solvent flow rate is reduced at 16 min, the model predicts a sudden decrease in the CO_2 capture rate due to the redistribution of liquid in the absorber column. Sudden drops in CO_2 capture rate were observed in the raw pilot plant data every 17 min due to purging of the outlet FTIR gas analysers. The raw pilot plant data has been processed to remove noise, consequently, these periodic fluctuations in CO_2 capture rate are absent in Fig. 7. At around 20 min, the CO_2 capture rate decreases from 97% to 90% in the raw plant data. However, it is unclear whether the cause of this sudden decrease is due to liquid redistribution in the absorber, or purging of the FTIR gas analysers. Generally, the modelled values of CO_2 capture rate are in agreement with the PACT plant data (Fig. 7).

4.2.3. Reboiler decoupling

The reboiler decoupling scenario demonstrates the effect of turning off the hot water supply to the reboiler (Table 5 and Table 15). During initial conditions, the hot water flow rate was 9.9 m^3/h, which translated to a reboiler temperature of 117.4 °C and CO_2 capture rate of 92.3%. At 0 min, the hot water supply to the reboiler was turned off (*i.e.*, flow = 0 m^3/h). Subsequently, reboiler temperature decreased gradually, which increased lean CO_2 loading and reduced CO_2 capture rate, shown in Figs. 9 and 10. The hot water flow to the reboiler is restored to 9.9 m^3/h at 118 min. Following this, the reboiler temperature increased (reaching values similar to initial conditions), resulting in decreased lean and rich CO_2 loading, and increased CO_2 capture rate.

The partial load stripping and capture plant ramping scenarios could be simulated without any model convergence issues as the process parameter changes were within the normal window of operation in the software. However, in the case of reboiler decoupling, simulating a step-change to 0 m^3/h hot water flow rate with the model was not feasible. Alternatively, the measured solvent CO_2 loading during zero hot water flow rate can be used as a model input. This approach involved implementing the trend observed for solvent CO_2 loading (blue circles in Fig. 9) into the model to simulate the dynamic behaviour of the reboiler decoupling scenario. Fig. 11 demonstrates the effect of reboiler decoupling on the absorber temperature profile. The predicted absorber temperature profile was in good agreement with the PACT plant measurements. The lean CO_2 loading had a strong impact on the absorber temperature (Fig. 11). As lean CO_2 loading increased (between 0 to 120 min), the absorber temperature profile shifted to lower temperatures–average APD 0.5–1.4% (Table 16). In contrast, the reduction in lean CO_2 loading (from 120 to 240 min) shifted the absorber temperature profile to higher temperatures (due to the exothermic nature of the CO_2 absorption reaction).

Fig. 10 shows the PACT data for CO_2 capture rate compared with the modelled gCCS predictions (values presented in Appendix B). For the reboiler decoupling scenario, the predicted CO_2 capture rate has a higher percentage difference compared to the previous two scenarios. Higher percentage difference tends to be associated with the lowest values of CO_2 capture rate, where the absolute difference represents a greater proportion of the PACT data value. From 140 min to 180 min, the absolute difference between the predicted CO_2 capture rate and PACT data was higher (7.5–10.3%), furthermore, average APD of absorber temperature predictions was also slightly higher 0.6–2.2% (Table 16). Generally, the gCCS model adequately predicts the dynamic trend of CO_2 capture rate over the duration of the reboiler decoupling scenario.

5. Conclusion

This study presents data from three dynamic operation scenarios implemented at the UKCCSRC PACT pilot plant, representative of realistic flexible operation of non-baseload CCS power plants. This dynamic plant data was used to validate a dynamic model developed in gCCS. For both steady state and dynamic model simulations, the dynamic model predictions of absorber temperature profile were in good agreement with the PACT pilot plant measurements. The model values for CO_2 capture rate closely concurred with PACT plant data in the case of the steady state simulations (% difference of 1.9–3.3%) and the capture plant ramping scenario (% difference of 0.33–1.8%). Higher deviations between the model values of CO_2 capture rate and PACT measurements were observed for the partial load stripping (% difference of 2.1–12.9%) and reboiler decoupling dynamic scenarios (% difference of 3.0–25.1%). For these scenarios, although the model could not replicate the exact CO_2 capture rate obtained in the pilot plant, the dynamic model successfully demonstrated the same transient behaviour observed in the pilot plant results.

Overall, the modelled dynamic response was in agreement with pilot plant trends. The discrepancies between the model predictions and the pilot plant results may be attributed to the assumption of ideal conditions in the model whereas operational data is subject to non-ideal factors. For instance, plant data may consist of outliers or fluctuate. Data processing techniques may be applied to "smooth" fluctuations in experimental measurement. Another possible factor that may contribute to model discrepancies is the constraints imposed by the software. The model is only able to simulate scenarios that remain within the feasible operating window of the software (specific for given process parameters). In the case of the reboiler decoupling scenario, zero hot water flow rate could not be implemented in the model. Instead, the transient trends of the CO_2 loading were implemented into the model to simulate the reboiler decoupling scenario.

The combination of pilot plant experiments and dynamic modelling has provided some valuable insight into the interaction between key process parameters in producing the dynamic response in a CO_2 capture process. Earlier studies show that L/G ratio has a significant impact on CO_2 capture rate (Artanto et al., 2012, 2014; Krótki et al., 2016; van de Haar et al., 2017). In the capture plant ramping scenario, increased L/G ratio resulted in higher CO_2 capture rate. When the flue gas and solvent flow rates were varied simultaneously, the L/G ratio was an important factor to consider as it had an impact on overall CO_2 capture performance. The L/G ratio remained constant in the partial load stripping and reboiler decoupling scenarios. The partial load stripping scenario demonstrated that the supply of heat directly affects the reboiler temperature, which in turn, has an impact on the lean CO_2 loading and CO_2 capture rate. This relationship is also demonstrated in the reboiler decoupling scenario. Once the heat supply to the reboiler was turned off, the reboiler temperature gradually declines. Subsequently, the lean CO_2 loading increased, which resulted in lower CO_2 capture rate.

The absorber column temperature profile is directly influenced by the degree of CO_2 capture. As the CO_2 absorption reaction is exothermic, the absorber temperature profile can be considered an indicator of CO_2 absorption performance. As shown by the reboiler decoupling scenario, reducing the lean solvent CO_2 loading shifts the absorber temperature profile to higher temperatures (due to higher rate of CO_2 capture). Conversely, absorber temperature profile of low temperature correspond to conditions of high lean CO_2 loading and low CO_2 capture rate. This work has contributed to the identification of key dynamic process properties and parameters important for flexible operation. Understanding the interaction between these process parameters will be essential for the development of robust control strategies for flexible operation in CO_2 capture plants.

The following considerations are important in improving process modelling capabilities to accurately describe flexible operation of CO_2 capture processes.

- Pilot plant data and models that describe a wide range of operating conditions—demonstrate transient behaviour for multiple process parameter changes and for a wide operating window. This is needed to improve model robustness, to enable evaluation of plant flexibility limits, and identify the actual minimum and maximum operating window.
- Dynamic experimental data from CO_2 capture plants of larger scale can be used develop accurate commercial-scale models.
- Integrated models of power plants with CO_2 capture that accurately describe flexible operation—integration of these into a energy system models can be used to evaluate the value of flexible CCS.
- Pilot plant operators and process modellers should work together in the design of experimental test campaigns. Collaboration can help provide data that will be useful for both experimentalist and theoretical modellers.

As more pilot plants conduct testing of dynamic or flexible operation, experimental data demonstrating dynamic behaviour will become more available, which could help facilitate the development of more robust dynamic models and control strategies.

Whilst there has been a lot of progress made in the area of dynamic and flexible operation for CO_2 capture, more work is necessary to address the remaining research challenges. Further research needs to examine the dynamics of an integrated CCS system, considering the response of the overall system consisting of a power plant integrated with CO_2 capture and compression. For instance, the effect of CO_2 compression on the capture plant dynamics and response time, in particular stripper pressure, is still unclear. Future work on flexible operation should focus on improving plant operability and flexibility. Research on solvent design should aim to improve fluid flow properties to ensure adequate flow and solvent distribution. Currently, CO_2 capture pilot plants tend to be configured for steady state operation. The online CO_2 loading measurement device in this work provided valuable dynamic data. Further work is needed to develop similar process measurement/monitoring tools specifically designed for dynamic conditions (*e.g.*, probe positioning strategies to improve measurement reliability). Additionally, process control strategies designed to improve operability during flexible operation is needed (*e.g.*, to increase operating window of process parameters). As more dynamic data from different pilot plants becomes available, further work could aim to formulate the fundamental relationship between plant scale and plant dynamics.

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Appendix A. Summary of studies on dynamic modelling of CO_2 capture

Table 6
Overview of recent studies on dynamic operation and modelling of post-combustion CO_2 capture with model validation against pilot plant data (in chronological order).

Reference	Research institute	Pilot plant validation data	Model description &Simulations conducted	Process simulation software
Enaasen et al. (2014)	NTNU (Norway), ENEL Engineering and Research Division (Italy) and SINTEF Materials and Chemistry (Norway)	Brindisi pilot plant (Italy) captures 1000–2500 kg_{CO_2}/h (2000 kg_{CO_2}/h design capacity using 30 wt% MEA). Dynamic pilot plant data used for model validation includes: CO_2 product flow rate, lean solvent loading, rich loading, CO_2 concentration at the absorber gas outlet, absorber temperature profile and the CO_2 capture rate.	Dynamic model of the Brindisi CO_2 capture pilot plant developed with a control scheme representative of the system employed in the plant. Model validated with dynamic data; steady state validation not presented. Simulations include: (1) Step changes in steam flow rate to reboiler, (2) Step changes in solvent flow, (3) Step changes in flue gas flow.	CO_2 capture process modelling in K-Spice general dynamic simulation tool, thermodynamic &physical properties provided by MultiFlash (InfoChem Ltd.) and CO2SIM software (SINTEF).
Enaasen Flø et al. (2015)	NTNU (Norway), ENEL Engineering and Research Division (Italy) and SINTEF Materials and Chemistry (Norway)	Gløshaugen (NTNU/SINTEF) pilot plant has a capacity of 12.5 kg_{CO_2}/h when operating with MEA solvent (Pinto et al., 2014). Steady state and dynamic plant data was used to validate the model.	Dynamic model of the pilot plant consists of various process unit/equipment models–developed from the first principle mass/energy balance equations.	MATLAB using ODE solver ODE15s.
Garðarsdóttir et al. (2015)	Chalmers University of Technology (Sweden) and Modelon AB (Sweden)	Esbjerg pilot plant located at the DONG Energy coal-fired power station in Denmark. The plant capture capacity is 1 t_{CO_2}/h using MEA solvent (Faber et al., 2011). Experimental dynamic test results include step changes in flue gas flow, solvent flow and steam flow rate to the reboiler. Effects on capture efficiency, column temperatures and CO_2 product flow were monitored.	Dynamic model of the integrated system comprises of: (1) CO_2 capture model validated against both steady state and dynamic data from the Esbjerg pilot plant. (2) A steady state model of the Nordjyllandsværket power plant with a capture system integrated in the steam cycle. Two flexible operation scenarios were investigated: part-load and peak load operation.	CO_2 capture modelled using the Modelica® modelling language and simulated using Dymola (Prölß et al., 2011; Åkesson et al., 2012). Steady state power plant model was developed in Ebsilon 7.0
Luu et al. (2015)	School of Chemical and Biomolecular Engineering, The University of Sydney (Australia)	Steady state model validation against column temperatures and stream conditions from the following: (i) SRP pilot plant at the University of Texas (200–250 kg_{CO_2}/h), case 32 &47 from Dugas (2006); (ii) Aspen model results from Harun (2012), (iii) Tarong pilot plant (100 kg_{CO_2}/h, Cousins et al., 2012) in Saimpert et al. (2013), (iv) pilot plant in Tontiwachwuthikul et al. (1992). Dynamic model validation was not conducted due the lack of dynamic data.	Mechanistic dynamic model of CO_2 capture adapted from various sources, includes absorber/stripper (Kvamsdal et al., 2009; Harun, 2012), reboiler and cross heat exchanger (Harun, 2012) and lean solvent storage (Nittaya et al., 2014b). Process control analysis of 3 proposed control schemes: standard PID feedback control, cascade-PID scheme, and a model predictive control (MPC) strategy. Of these, the MPC strategy was able to handle disturbances during flexible operation.	gPROMS (Process Systems Enterprise, Ltd.)
Enaasen Flø et al. (2016)	NTNU (Norway) and SINTEF Materials and Chemistry (Norway)	Brindisi pilot plant in Italy (design capacity of 2000 kg_{CO_2} using 30 wt% MEA). Dynamic data and validation of this model presented in earlier work by Enaasen et al. (2014)	Using the model developed in Enaasen et al. (2014), the following scenarios were evaluated: (i) load following, (ii) exhaust gas venting, (iii) varying steam flow rate (changes the degree of solvent regeneration), and (iv) solvent storage.	K-Spice® general simulation tool
Wellner et al. (2016)	Hamburg University of Technology (Germany)	Pilot plant Heilbronn (Germany) is a post-combustion capture process with the capacity to capture 300 kg_{CO_2}/h at 90% capture rate (Rieder and Unterberger, 2013). Steady state and transient tests were conducted.	CO_2 capture model was validated against both steady state and dynamic data. This capture model was coupled with a power plant model to simulate the impact of reducing steam extraction (from full load operation, then reducing steam flow by 50%).	The dynamic model is developed using modelling language Modelica®. The *ThermalSeparation* model library provides the basis for the CO_2 capture model, whereas *ClaRa* is used to for the water-steam cycles.
Chinen et al. (2016)	Department of Chemical Engineering, West Virginia University (US), and National Energy Technology Laboratory (US)	Steady state and dynamic pilot plant data was collected from the National Carbon Capture Centre (NCCC) – reported capacity between 80–800 kg_{CO_2}/h (Cousins et al., 2016). To address measurement uncertainty issues in dynamic data, a “dynamic data reconciliation” (DDR) framework was developed to ensure that material & energy balances are closed.	Steady-state MEA-based CO_2 capture plant is modelled in Aspen Plus. The dynamic model was first developed in Aspen Plus before being exported to Aspen Plus Dynamics. The focus of this work was to establish a robust reference model for a large operating range.	Aspen Plus and Aspen Plus Dynamics. Some submodels are implemented as FORTRAN user models.

(*continued on next page*)

Table 6 (*continued*)

Reference	Research institute	Pilot plant validation data	Model description &Simulations conducted	Process simulation software
Abdul Manaf et al. (2016)	School of Chemical and Biomolecular Engineering, The University of Sydney (Australia) and CSIRO Energy (Australia)	Dynamic data from the Tarong pilot plant (capture capacity of 100 kg_{CO_2}/h (Cousins et al., 2012)) was used to develop data-driven models of each unit operation.	Black-box modelling approach, using a multi-variable non-linear autoregressive with exogenous input (NLARX) model, was developed to evaluate the dynamics of an MEA-based CO_2 capture pilot plant — characterised as a multiple input multiple output system and non-linear process. Individual unit models were developed (data-driven) and integrated to generate various process configurations, which were used to analyse controllability.	Model was developed in the Simulink workspace. Individual process model exported to the Simulink workspace using a Nonlinear ARX model block function (chosen to imitate the NLARX data driven model).
Gaspar et al. (2016a)	Technical University of Denmark (Denmark), and University of Waterloo (Canada)	Design of pilot plant resembles specification of the Esbjerg pilot plant in Faber et al. (2011), which captures 1000 kg_{CO_2}/h. MEA-based data was available for both steady state and dynamic conditions. However, only steady state data was available for the piperazine-based process (Gaspar et al., 2015, 2016b,c). Key validation data includes absorber CO_2 outlet concentrations, CO_2 removal rates and absorber/stripper temperature profiles.	The dCAPCO2 rate-based model was implemented in Matlab (Gaspar et al., 2016b,c) and uses the extended UNIQUAC thermodynamic model (Faramarzi et al., 2009) and the GM enhancement factor model (Gaspar and Fosbøl, 2015). A decentralised PI-control structure is developed based on Relative Gain Array analysis. Controllability and flexibility of CO_2 capture processes for two solvent systems, piperazine and MEA is evaluated and compared.	MATLAB using the ODE15s solver
Montañés et al. (2017)	Norwegian University of Science and Technology, NTNU (Norway) and CO_2 Technology Center Mongstad, TCM (Norway)	Steady state and dynamic plant data was acquired from the Technology Centre Mongstad (TCM) CO_2 capture plant. Combined heat and power (CHP) operation was used during this test campaign, where the capture capacity was 80 t_{CO_2}/day and flue gas CO_2 concentration was 3.5 vol%.	Dynamic model based on conventional amine-based configuration. Key consideration of the model was size, geometry and materials of the main process equipment — describes distribution of solvent inventory. To validate the model, simulations included: (i) steady state scenarios for validation, (ii) flue gas flow rate ramp down, (iii) flue gas flow rate ramp up with step-changes to reboiler duty, (iv) rich solvent flow rate ramp down. The model was then used to analyse open-Loop performance and test different decentralised control structures.	Model developed using modelling language Modelica®, where process equipment models were from the Modelica library called Gas Liquid Contactors. Dymola (Dassault Systèmes) was used to simulate the model with the differential algebraic system solver (DASSL).

Table 7
Experimental studies testing dynamic operation of post-combustion CO_2 capture in pilot plants.

Reference	Pilot plant site	Capture capacity	Flue gas source	Dynamic operation scenarios
Faber et al. (2011)	Esbjerg pilot plant, DONG Energy Esbjergværket power plant, Denmark	1 t_{CO_2}/day using MEA solvent	Coal-fired power station	Plant operated in open-loop control to minimise effect of control loops. The following scenarios were tested: (i) decrease/increase step-change of flue gas flow rate, (ii) decrease/increase step change of steam flow rate to the reboiler, (iii) decrease/increase solvent flow rate, (iv) simultaneous decrease/increase of flue gas flow rate, steam flow rate and solvent flow rate.
Mangiaracina et al. (2014)	Brindisi pilot plant, ENEL Federico II coal power plant, Italy	50 t_{CO_2}/day using 30 wt% MEA	Coal-fired power station	Pilot plant campaign of six weeks, where the following tests were completed: (i) solvent storage cycle – effect of storage tanks; (ii) maximum speed stripping – highest solvent flow rate and steam flow rate; (iii) stripping from cold start – rich solvent produced, plant shut-down and cooled, then attempted to regenerate from cold start; (iv) super lean solvent production &capture performance – effect of over stripping the solvent.
de Koeijer et al. (2018)	CO_2 Technology Centre Mongstad (TCM), Norway	80 t_{CO_2}/day (CHP configuration) using 30 wt% MEA	Combined heat and power plant (CHP): flue gas CO_2 content of 3.4–3.6 mol%	Two transient cases were presented: (i) Controlled stop and restart of flue gas and steam flow rate, with a period of no flue gas flow and recirculation flow maintained. (ii) Sudden stop of inlet exhaust gas blower and rapid restart with constant steam flow and solvent flow. Studied impact on MEA and NH_3 emissions from absorber, also CO_2 product flow rate and temperature.
Bui et al. (2016a)	CSIRO PCC pilot plant at AGL Loy Yang A power station, Australia	0.48 t_{CO_2}/day using MEA solvent	Brown coal-fired power station	The test campaign studied the effect of successive step-changes to: (i) flue gas flow rate, (ii) solvent flow rate, and (iii) steam flow rate to the reboiler. The study analysed the effect on the absorber/stripper temperature profile, CO_2 concentration of the lean and rich solvent, CO_2 removal rate and reboiler heat duty.
Tait et al. (2016)	Pilot-scale facilities of Sulzer Chemtech in Winterthur, Switzerland	0.17 t_{CO_2}/day using 30 wt% MEA	Synthetic flue gas composed of N_2 and CO_2. For this test, 4.3 vol% CO_2 content was used to represent NGCC exhaust.	Five dynamic scenarios representative of NGCC operation with CO_2 capture: (i) gas turbine shut-down, (ii) gas turbine start-up, (iii) maximise power output by decoupling capture plant, (iv) maximise power output by decoupling the reboiler steam only, and (v) rapid increase of reboiler steam flow rate (200% baseload flow).
Tait et al. (2018)	UKCCSRC PACT CO_2 capture pilot plant, University of Sheffield, United Kingdom	1 t_{CO_2}/day using 30 wt% MEA	Synthetic flue gas from air and CO_2. Inlet gas CO_2 concentration for this test was 12 vol% (simulates exhaust from coal-fired power plant).	The scenarios were designed to represent dynamic operation in a supercritical coal-fired power plant with post-combustion capture: (i) generation plant shut-down, (ii) generation plant start-up (tested two options), (iii) partial load stripping (reduce hot water flow to reboiler), (iv) capture bypass by decoupling hot water flow, (v) capture plant ramping, and (v) control capture efficiency using online solvent measurements.
Montañés et al. (2018)	CO_2 Technology Centre Mongstad (TCM), Norway	80 t_{CO_2}/day (CHP configuration) using 30 wt% MEA	Combined heat and power plant (CHP): flue gas CO_2 content of ∼4 vol% (wet)	Tests on open-loop performance were conducted first. This involved implementing single step-changes to the flue gas flow rate and solvent flow rate. The second phase studied the performance of decentralised control structures, different tests were carried to: (i) control L/G ratio and stripper bottom temperature, and (ii) control capture rate.

Appendix B. Specifications of the UKCCSRC PACT CO_2 capture plant

Table 8
Column and packing specifications.

Specification	Absorber	Stripper	Water wash
Geometry	Cylindrical	Cylindrical	Cylindrical
Packing height (m)	6.5	6.1	1.2
Diameter (m)	0.30	0.30	0.30
Sump volume (L)	70	400	–
Pressure	Atmospheric	120–300 kPa abs	Atmospheric
Packing type	Sulzer Mellapak CC3 (structured)	IMTP 25 (random)	IMTP 25 (random)
Material of packing	Metal	Metal	Metal
Specific area (m^2/m^3)	250	207	207
Void fraction	0.980	0.970	0.970
Nominal size (m)	–	0.025	0.025

Table 9
Typical synthetic flue gas composition at absorber inlet.

Flue gas component	Composition (vol%)
N_2	67.7
CO_2	12.3
H_2O	1.0
O_2	18.2
Ar	0.80

Appendix C. PACT pilot plant datasets

Table 10
Steady state data – two cases from the PACT pilot plant.

Specification	Case A	Case B
Flue gas flow rate (Nm^3/h)	199.2	199.4
Lean solvent flow (kg/h)	974.3	1181.7
L/G ratio (kg liq/Nm^3 gas)	4.89	5.93
Feed flue gas CO_2 concentration (vol%)	12.3	12.0
Feed flue gas H_2O concentration (vol%)	1.0	1.1
Absorber flue gas inlet temperature (°C)	45.2	45.9
Absorber solvent inlet temperature (°C)	40.2	40.1
Stripper solvent inlet temperature (°C)	100.5	97.7
Stripper pressure (kPa abs)	147	151
Reboiler temperature (°C)	118.1	116.3
MEA concentration (wt%)	30.4	30.6
Lean CO_2 loading (mol CO_2/mol MEA)	0.1290	0.2359
Rich CO_2 loading (mol CO_2/mol MEA)	0.3700	0.4115
PACT plant CO_2 capture rate (%)	91.2	86.8
Absorber packing height from base (m)	Temp (°C)	Temp (°C)
0.11	42.2	42.0
0.81	47.5	47.6
1.50	54.1	53.5
2.20	58.4	56.7
2.89	62.7	60.4
3.59	67.4	64.0
4.29	70.9	67.2
4.98	71.4	66.6
5.68	65.1	57.7
6.37	54.5	48.6

Table 11
Steady state model validation of the absorber temperature profile. Note that the absolute percentage deviation (APD) is calculated based on temperature units of kelvin.

Absorber packing height from base (m)	Case A				Case B			
	PACT Temp (°C)	gCCS Temp (°C)	Absolute deviation (K)	APD (%)	PACT Temp (°C)	gCCS Temp (°C)	Absolute deviation (K)	APD (%)
0.11	42.2	47.2	4.9	1.6	42.0	49.5	7.5	2.4
0.81	47.5	55.1	7.6	2.4	47.6	57.0	9.5	2.9
1.50	54.1	60.1	6.0	1.8	53.5	61.4	7.9	2.4
2.20	58.4	63.8	5.4	1.6	56.7	64.4	7.7	2.3
2.89	62.7	66.9	4.2	1.3	60.4	66.7	6.4	1.9
3.59	67.4	69.4	2.0	0.6	64.0	68.4	4.4	1.3
4.29	70.9	71.3	0.4	0.1	67.2	69.0	1.8	0.5
4.98	71.4	71.8	0.3	0.1	66.6	67.7	1.1	0.3
5.68	65.1	68.7	3.6	1.1	57.7	62.3	4.6	1.4
6.37	54.5	57.9	3.4	1.0	48.6	51.7	3.0	0.9
Average			3.8	1.2			5.4	1.6

Table 12
Dynamic scenario – partial load stripping.

Time (min)	0	140	250
Flue gas flow rate (Nm^3/h)	200.0	200.0	199.9
Lean solvent flow rate (kg/h)	985.8	990.9	985.5
L/G ratio (kg liq/Nm^3 gas)	4.93	4.95	4.93
Hot water flow rate (m^3/h)	10.0	5.0	10.0
Reboiler temperature (°C)	117.4	114.9	118.1
Lean CO_2 loading (mol CO_2/mol MEA)	0.1741	0.2781	0.1632
Rich CO_2 loading (mol CO_2/mol MEA)	0.3688	0.4164	0.3501
PACT plant CO_2 capture rate (%)	93.7	77.3	95.5
Feed flue gas CO_2 concentration (vol%)	12.2	12.2	12.4
Absorber flue gas inlet temp (°C)	45.6	46.4	46.3
Absorber solvent inlet temp (°C)	40.1	39.7	40.3
Stripper solvent inlet temp (°C)	98.4	96.5	99.6
Stripper pressure (kPa abs)	148	150	147

Table 13
Partial load stripping scenario – PACT pilot plant data for absorber temperature.

Time (min)	−20	0	20	40	60	80	120	140	160	180	200	220	250
Reboiler T (°C)	117.4	117.4	116.8	116.1	115.3	115.3	115.3	114.9	116.9	117.4	117.7	117.8	118.1
PACT capture %	92.0	93.7	93.7	86.4	81.3	76.8	77.8	77.3	83.2	91.1	93.8	94.6	95.5
gCCS capture %	90.8	90.8	84.1	77.4	71.6	66.8	66.8	66.8	70.5	76.1	82.5	89.5	91.7
Difference	1.2	2.9	9.7	9.0	9.7	10.0	11.0	10.5	12.7	14.9	11.3	5.1	3.9
% Difference	1.3	3.1	10.3	10.4	12.0	13.0	14.2	13.6	15.3	16.4	12.0	5.4	4.0
PACT Reb duty (MJ/kg CO_2)	5.61	5.65	3.89	4.86	3.37	5.73	5.14	4.38	6.15	5.95	5.51	5.66	5.87
gCCS Reb duty (MJ/kg CO_2)	3.68	3.68	3.55	3.48	3.45	3.57	3.57	3.57	3.57	3.58	3.61	3.71	3.70
Packing height from base (m)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)
0.11	44.1	44.6	44.5	42.8	41.5	41.4	41.0	40.7	42.3	44.1	44.9	45.2	45.5
0.81	50.3	50.8	50.8	48.4	46.9	46.0	45.9	45.6	47.7	49.9	51.1	51.7	52.1
1.50	56.8	57.7	57.4	54.5	53.2	52.1	51.7	51.5	53.9	56.6	58.1	58.6	59.0
2.20	61.1	61.9	61.7	58.0	56.3	55.2	54.7	54.5	57.6	60.5	62.6	62.9	63.7
2.89	64.6	65.5	65.7	61.6	59.5	58.3	57.8	57.6	61.0	64.3	66.6	66.8	67.6
3.59	68.2	68.9	69.0	65.0	62.7	61.3	60.9	60.9	64.6	67.9	69.8	70.1	70.5
4.29	70.7	71.2	71.4	68.4	66.0	64.5	64.0	64.2	67.5	70.7	71.9	72.0	72.2
4.98	69.5	69.3	69.7	67.9	66.2	64.8	64.4	64.4	67.2	69.2	70.6	70.3	70.4
5.68	58.9	57.3	59.0	59.1	58.4	57.4	56.7	57.0	57.0	59.4	59.5	59.3	58.8
6.37	47.9	47.3	47.4	48.8	48.8	48.3	48.9	48.5	49.1	48.2	50.1	48.4	48.4
Average absolute deviation (K)	2.4	2.4	2.2	2.4	2.7	3.0	3.2	3.3	2.4	2.2	2.3	2.0	2.0
Average APD (%)	0.74	0.73	0.67	0.73	0.84	0.91	0.99	1.0	0.73	0.67	0.69	0.60	0.60

Table 14
Dynamic scenario – capture plant ramping.

Time (min)	0	100	200
Flue gas flow rate (Nm^3/h)	198.7	137.7	199.5
Lean solvent flow rate (kg/h)	999.9	706.9	974.4
L/G ratio (kg liq/Nm^3 gas)	5.03	5.13	4.88
Hot water flow rate (m^3/h)	10.0	7.0	10.0
Reboiler temperature (°C)	117.7	117.9	118.1
Lean CO_2 loading (mol CO_2/mol MEA)	0.1322	0.1211	0.1286
Rich CO_2 loading (mol CO_2/mol MEA)	0.3995	0.3508	0.3639
PACT plant CO_2 capture rate (%)	91.0	95.1	90.0
Feed flue gas CO_2 concentration (vol%)	12.4	12.0	12.2
Absorber flue gas inlet temp (°C)	43.6	38.9	44.8
Absorber solvent inlet temp (°C)	39.9	39.9	40.0
Stripper solvent inlet temp (°C)	99.5	101.9	100.3
Stripper pressure (kPa abs)	147	149	148
PACT Reb duty (MJ/kg CO_2)	5.70	6.26	5.65
gCCS Reb duty (MJ/kg CO_2)	3.63	3.56	3.58
ABS packing height from base (m)	*T* (°C)	*T* (°C)	*T* (°C)
0.11	41.7	43.1	42.2
0.81	47.2	49.0	47.5
1.50	53.7	55.9	54.1
2.20	57.9	61.3	58.5
2.89	61.9	66.8	62.7
3.59	66.9	70.4	67.4
4.29	70.3	72.0	70.8
4.98	70.9	70.2	71.3
5.68	64.7	61.1	64.7
6.37	53.9	45.0	54.2
Average absolute deviation (K)	4.3	2.7	3.3
Average APD (%)	1.3	0.83	1.0

Table 15
Reboiler decoupling scenario – PACT pilot plant process data.

Time (min)	−10	0	20	40	60	80	100	120	140	160	180	200	220	240
Hot water flow (m^3/h)	9.9	1.3	0.33	0.31	0.29	0.29	0.28	9.4	10.0	9.9	10.0	10.0	10.0	10.0
Reboiler temp (°C)	117.4	117.6	104.9	94.4	84.6	75.3	67.1	74.7	100.3	111.5	115.6	116.7	117.2	117.5
Flue gas flow (Nm^3/h)	200.8	200.1	198.7	199.3	199.9	199.8	199.6	199.9	200.0	200.2	200.2	199.8	199.7	200.6
Lean solvent flow (kg/h)	1113.5	1002.4	995.3	997.9	1011.0	1017.7	1029.1	1011.3	1008.8	1011.4	1012.6	1004.5	998.5	996.1
L/G ratio (kg liq/Nm^3 gas)	5.55	5.01	5.01	5.01	5.06	5.09	5.15	5.06	5.04	5.05	5.06	5.03	5.00	4.97
Lean CO_2 loading (mol/mol)	0.2259	0.1775	0.2735	0.3815	0.4427	0.4464	0.4544	0.4706	0.4243	0.3344	0.2274	0.2071	0.2114	0.1613
FG CO_2 conc (vol%)	12.5	12.4	12.3	11.9	11.6	11.9	12.0	11.8	12.0	12.0	12.1	12.3	12.0	11.9
ABS flue gas inlet temp (°C)	43.7	43.3	44.2	42.7	42.8	41.8	41.2	41.3	41.2	41.2	41.4	41.4	41.9	42.1
ABS solvent inlet temp (°C)	39.9	40.2	39.0	39.2	40.2	39.8	40.2	38.4	39.5	40.2	39.8	39.3	39.1	39.7
Stripper inlet temp (°C)	98.5	98.6	91.7	79.6	73.2	64.0	57.6	54.4	77.2	88.7	92.9	94.9	99.2	99.5
Stripper pressure (kPa abs)	146	143	106	101	101	101	101	104	147	144	146	145	144	144

Degree of deviation calculation

Absolute deviation demonstrates the degree of deviation between the pilot plant data and model predictions in terms of kelvin, *i.e.* vertical distance between model and plant data absorber temperature profiles (*e.g.*, in Fig. 3). The absolute percentage deviation (APD):

$$\mathrm{APD} = 100\left|\frac{T_m - T_p}{T_p}\right| \tag{1}$$

where T_m is the model prediction of temperature and T_p is the pilot plant value. For each case/scenario, the mean of these APD values is calculated and referred to as the average absolute percentage deviation (average APD). Both APD and average APD are calculated based on temperature units of kevin (K).

Table 16
Reboiler decoupling scenario – PACT pilot plant data for absorber temperature.

Time (min)	−10	0	20	40	60	80	100	120	140	160	180	200	220	240
PACT CO_2 capture rate (%)	92.3	89.9	70.3	39.1	22.6	12.2	8.9	7.6	15.0	43.3	71.8	86.3	92.6	95.0
gCCS CO_2 capture rate (%)	85.1	87.2	67.2	32.5	17.0	11.0	7.5	5.5	7.5	40.1	61.5	82.2	88.6	90.6
Difference	7.2	2.7	3.0	6.6	5.6	1.2	1.4	2.1	7.5	3.2	10.3	4.2	4.0	4.3
Percentage difference (%)	7.8	3.0	4.3	16.9	24.9	10.0	15.3	28.1	50.1	7.5	14.3	4.8	4.3	4.6
Packing height from base (m)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)
0.11	42.7	41.9	40.2	35.8	33.3	31.7	31.0	30.5	31.2	33.7	37.7	40.4	42.1	43.2
0.81	49.9	47.4	44.7	39.5	36.5	34.2	33.6	32.8	33.9	37.4	42.1	45.5	47.9	49.4
1.50	55.9	53.3	50.3	44.3	40.2	37.8	36.8	35.8	37.4	41.9	47.6	52.2	54.2	56.2
2.20	59.3	57.4	53.1	46.3	41.4	38.6	37.5	36.5	38.5	43.7	50.6	55.6	58.5	60.8
2.89	63.3	61.4	56.6	48.8	43.5	40.1	39.2	37.8	40.2	46.5	54.3	59.5	63.4	65.4
3.59	66.5	65.7	60.0	50.9	44.6	40.9	39.9	38.4	41.2	48.9	57.8	64.0	67.5	69.4
4.29	68.8	69.4	63.2	52.5	45.0	41.5	40.1	38.7	42.3	51.4	61.5	67.5	70.6	71.8
4.98	65.6	70.2	64.9	52.9	44.6	41.4	40.2	38.4	42.7	52.8	62.8	68.4	70.4	71.3
5.68	54.1	64.5	60.4	48.8	43.3	40.9	39.9	38.2	42.3	49.8	57.7	61.9	62.6	62.7
6.37	45.6	53.5	51.3	45.2	41.6	40.1	39.7	38.3	41.2	45.7	48.7	50.8	53.0	52.5
Average absolute deviation (K)	3.2	4.6	4.3	3.7	2.1	1.6	1.7	1.7	2.6	7.0	5.8	4.9	3.6	3.1
Average APD (%)	0.98	1.4	1.3	1.2	0.68	0.53	0.55	0.55	0.83	2.2	1.8	1.5	1.1	0.95

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